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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Concentration of Fatty Acids in Aqueous Solution and to the Recovery of said Acids from Aqueous Solutions thereof by Azeotropic Distillation

We, THE BRITISH PETROLEUM COMPANY LIMITED, previously known as Anglo-Iranian Oil Company Limited), of Britannic House, Finsbury Circus, London, E.C.2, a British Joint-Stock Corporation and WILFRED SAMUEL NATHAN and TIMOTHY ARROWSMITH RAYNE, both of the Company's Research Station, Chertsey Road, Sunbury-on-Thames, Middlesex, and both of British Nationality, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the concentration of fatty acids in aqueous solution and for the recovery of fatty acids from aqueous solution in the anhydrous state.

A process has hitherto been described in which fatty acids in dilute solution are concentrated by liquid/liquid solvent extraction using, as solvent, a mixture containing a hydrocarbon and an aliphatic ketone, thereafter distilling the extract, containing fatty acid in the presence of a diminished amount of water, to obtain an overhead fraction containing water and solvent, allowing the condensate to separate into two layers and returning the layer containing solvent to the mixture undergoing distillation. It is apparent that the above process requires the use of two separate process units, that is a liquid/liquid solvent extraction unit and a distillation unit, said distillation unit receiving solvent in admixture with a fatty acid solution which has already received a substantial concentration treatment in said solvent extraction unit.

It has now been found that provided the overhead fraction, referred to hereinbefore, is condensed and treated for the recovery of an upper phase, containing solvent, and said upper phase is recycled to the column head, it is possible to maintain in the upper part of the column sufficient solvent and hydrocarbon to ensure that a ketone/water/hydrocarbon azeotrope is removed overhead. Operating in this manner it has been found that fatty acid aqueous solutions of any concentration may be treated in economic manner for the removal of water in a single stage distillation operation.

It is an object of the present invention to provide an improved process for the concentration of fatty acids in aqueous solution. It is a further object to provide an improved process for the recovery of fatty acids, from aqueous solution, in the anhydrous state.

According to the present invention, an aqueous solution comprising one or more fatty acids having 1—4 carbon atoms/molecule is fractionally distilled in a distillation column operated in continuous manner in the presence of an aliphatic ketone having 4—7 carbon atoms/molecule and a volatile hydrocarbon, whereby an overhead product is removed comprising said ketone, said volatile hydrocarbon and water, thereafter condensing said overhead fraction, separating the condensed fraction into a lower phase comprising water and ketone and an upper phase comprising ketone and hydrocarbon, recycling said upper phase to the head of said column, distilling said lower phase for the concentration of ketone contained therein and blending the recovered ketone with the aqueous solution of fatty acid fed to the distillation column.

Preferred ketones are butanone, 2-methylbutanone-3, pentanone-2 and pentanone-3. Other suitable ketones are the hexanones and heptanones.

Preferably volatile hydrocarbons are employed which boil within the range 0—10° C. below the boiling point of the ketone.

When using butanone, the preferred volatile hydrocarbons are benzene and cyclohexane. When using a C_6 ketone, the preferred volatile hydrocarbons are methylcyclohexane and *n*-heptane. Other preferred hydrocarbons for use with C_4 or C_5 ketones are paraffin hydrocarbons or mixtures of paraffin hydrocarbons boiling over a range of not more

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than 10° C. and preferably over a range of not more than 5° C.

In accordance with preferred procedure, hexanones and higher ketones are not employed for the treatment of solutions of formic acid or acetic acid or fatty acid solutions comprising formic and/or acetic acid. In the presence of formic acid, pentanones are not usually employed, 2-butanone being the preferred ketone. However, if pentanones or hexanones are used for the treatment of acid mixtures containing formic and acetic acids and higher molecular weight acids (although they boil at about the same temperatures as the anhydrous formic and acetic acids) it is desirable to allow traces of water to penetrate below the level of the entrainer in the stripping section of the column. The bottom few plates of the column are then employed in stripping this residual trace of water by straight distillation.

By the process of the present invention there is provided means for effecting an azeotropic water removal process with efficient recovery of the ketone therein employed.

The process of the invention is illustrated but in no way limited with reference to the drawing accompanying the provisional specification.

With reference to said drawing:—

Aqueous fatty acids are introduced by line (9) and are passed together with recycled aqueous ketone, introduced by line (10), through preheater (1) to drying column (2). Dried acids are removed from the column base by line (11) and divided into two streams. One stream is circulated through reboiler (3) and the other passes through a cooler (4) and is then withdrawn from the system by line (12). The distillate is removed by line (13) and passes through condenser (5) into separator (6), the upper ketone and hydrocarbon layer being returned to the column head by line (14). The lower, aqueous phase passes by line (15) to stripping column (7) to which steam is fed by line (19). An azeotropic mixture of ketone and water is removed overhead from column (7) by line (16) and is passed to condenser (8). Part of the condensed aqueous ketone is returned as reflux to column (7) by line (17) and part recycled by line (10) to the feed of aqueous acids entering the system. The stripped water from the base of column (7) is run to waste by line (18).

The invention is further illustrated but in no way limited by the following examples.

EXAMPLE I

Operating in the manner described with reference to the drawing accompanying the provisional specification and using butanone (methyl ethyl ketone) and cyclohexane as the ketone and volatile hydrocarbon respectively, an aqueous acid mixture of the following composition was fed at 100 ml per hour, to a fractionating column of 40 theoretical plates with feed admitted at the 20 theoretical plate level.

COMPOSITION OF FEED

Formic acid	70 grams
Acetic Acid	630 grams
Water	300 grams

Column temperatures were:—

Top	66.5° C.
Feed level	100° C.
Base	100.5° C.

Aqueous phase was removed from the separator (6) at 34 ml./hr. and contained 9.0% by weight of butanone in solution. This dissolved ketone was stripped from the waste water in column (7) as a ketone/water azeotrope (b.p. 73° C.) which was returned to the system with the aqueous acids fed to the main column. The waste water was quite neutral and contained no detectable quantity of formic acid or acetic acid.

The dried acid contained:—

Butanone less than	0.25% by weight
Water	0.32% by weight

The overhead product contained (as % by weight thereof):—

	Upper phase	Lower phase
Butanone	37.3	0.78
Cyclohexane	53.85	0.17
Water	2.65	5.25

What we claim is:—

1. A process for the concentration of fatty acids in aqueous solution which comprises fractionally distilling an aqueous solution comprising one or more fatty acids having 1—4 carbon atoms/molecule in a distillation column operated in continuous manner in the presence of an aliphatic ketone having 4—7 carbon atoms/molecule and a volatile hydrocarbon, whereby an overhead product is removed comprising said ketone, said volatile hydrocarbon and water, thereafter condensing said overhead fraction, separating the condensed fraction into a lower phase comprising water and ketone and an upper phase comprising ketone and hydrocarbon, recycling said upper phase to the head of said column, distilling said lower phase for the concentration of ketone contained therein and blending the recovered ketone with the aqueous solution of fatty acid fed to the distillation column.

2. A process according to Claim 1 in which the volatile hydrocarbon boils at the boiling point of the ketone or not more than 10° C. below said boiling point.

3. A process according to Claim 1 or 2 in which the ketone is butanone.

4. A process according to Claim 3 in which the volatile hydrocarbon is benzene.

5. A process according to Claim 3 in which the volatile hydrocarbon is cyclohexane.

6. A process according to Claim 1 in which the ketone has five carbon atoms/molecule.

7. A process according to Claim 6 in which the volatile hydrocarbon is methylcyclohexane.

8. A process according to Claim 6 in which the volatile hydrocarbon is normal heptane.

9. A process according to any of the preceding claims in which the ketone is a C_4 or C_5 ketone and in which the volatile hydrocarbon is a paraffin hydrocarbon or in which there is used a mixture of paraffin hydrocarbons boiling over a range of not more than 5° C.

10. A process for the concentration of fatty acids in aqueous solution substantially as hereinbefore described with reference to the drawing accompanying the provisional specification.

11. Fatty acids wherever concentrated by a process as claimed in any of claims 1—10.

T. MACDONALD,
For the Applicants.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Concentration of Fatty Acids in Aqueous Solution and to the Recovery of said Acids from Aqueous Solutions thereof by Azeotropic Distillation

We, ANGLO-IRANIAN OIL COMPANY, LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation and WILFRED SAMUEL NATHAN and TIMOTHY ARROWSMITH RAYNE, of the aforesaid Company's address, and both of British nationality, do hereby declare this invention to be described in the following statement:—

This invention relates to an improved process for the concentration of fatty acids in aqueous solution and for the recovery of fatty acids from aqueous solution in the anhydrous state.

It is known that organic acids may be recovered from dilute aqueous solutions by distillation in the presence of an entrainer to remove water overhead. A process has been described in French Specification No. 856,562 for the removal of water from aqueous acetic acid in which ethyl acetate is employed as the entrainer, a quantity of low boiling hydrocarbon being maintained in the upper part of the distillation column while distillation is in progress. It has been found that ethyl acetate is limited, in its application to the dehydration of fatty acids, to the treatment of acetic acid since, in the presence of other members of the series, an ester-interchange reaction takes place which leads to loss of the entrainer.

It is an object of the present invention to provide an improved process for the concentration of fatty acids in aqueous solution. It is a further object to provide an improved process for the recovery of fatty acids, from aqueous solution, in the anhydrous state.

According to the present invention, an aqueous solution comprising one or more fatty acids is fractionally distilled in the presence of an aliphatic ketone whereby an azeotrope comprising the ketone and water is removed as an overhead fraction.

Preferred ketones are 2-butanone, pentanones and hexanones. When these ketones are employed it has been found very advantageous to maintain, in the distillation column, a quantity of a volatile hydrocarbon, whereby a ketone/water/hydrocarbon azeotrope is removed overhead. Preferably volatile hydrocarbons are employed which boil with 10° C. of the boiling point of the ketone.

When using 2-butanone, the preferred volatile hydrocarbons are benzene, cyclohexane, paraffin hydrocarbons and mixtures of paraffin hydrocarbons boiling over a narrow range of not more than 10° C. but preferably 5° C.

Hexanones and higher ketones are not generally suitable for the treatment of solutions of formic acid or acetic acid or fatty acid solutions comprising formic and/or acetic acid. In the presence of formic acid, pentanones are not generally suitable, 2-butanone being the preferred ketone.

The overhead product obtained by distillation when operation in the absence of a volatile hydrocarbon may be separated into an upper layer consisting essentially of the ketone, which is recycled for treating further quantities of feedstock, and a lower aqueous layer containing some ketone. This aqueous layer may be treated by stripping or by solvent extraction for the recovery of the ketone for recycling.

When operating in the presence of a volatile hydrocarbon, the overhead product, on condensing, forms two phases. The lower, aqueous layer is removed and the upper layer, consisting essentially of the hydrocarbon and ketone and being substantially free of water, is returned to the top of the distillation column.

The process of the invention is particularly suitable for continuous operation.

The process of the invention is illustrated but in no way limited by the accompanying Figure

With reference to said figure:—

Aqueous fatty acids are introduced by line (9) and are passed together with recycled ketone, introduced by line (10), through preheater (1) to drying column (2). Dried acids are removed from the column base by line (11) and divided into two streams. One stream is circulated through reboiler (3) and the other passes through a cooler (4) and is then withdrawn from the system by line (12). The distillate is removed by line (13) and passes through condenser (5) into separator (6), the

upper ketone layer being returned to the column head by line (14). The lower, aqueous phase passes by line (15) to stripping column (7) to which steam is fed by line (19). Ketone is removed overhead from column (7) by line (16) and is passed to condenser (8). Part of the condensed ketone is returned as reflux to column (7) by line (17) and part recycled by line (10) to the feed of aqueous acids entering the system. The stripped water from the base of column (7) is run to waste by line (18).

The invention is further illustrated but in no way limited by the following example.

EXAMPLE

Operating in the manner described with reference to the accompanying figure and using butanone and cyclohexane as the ketone and volatile hydrocarbon respectively, an aqueous acid mixture of the following composition was fed to the system at 100 ml. per hour.

COMPOSITION OF FEED

Formic acid - - - -	70 grams
Acetic Acid - - - -	630 grams
Water - - - - - -	300 grams

Aqueous phase was removed from the separator (6) at 34 ml./hr. and contained 9.0% by weight of butanone in solution. This dissolved ketone was stripped from the waste water in column (7) as a ketone/water azeotrope (b.p. 73° C.) which was returned to the system with the aqueous acids fed to the main column. The waste water was quite neutral and contained no detectable quantity of formic acid or acetic acid. The water content of the dried acid from the base of column (2) was found to vary between 0.21—0.33% by weight when determined by Fischer Reagent and to contain no detectable quantity of butanone.

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For the Applicants.

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735,867 PROVISIONAL SPECIFICATION
1 SHEET

This drawing is a reproduction of the Original on a reduced scale.